



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

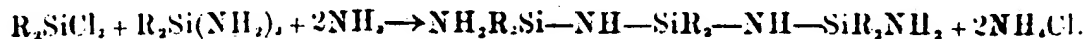
### Improvements and relating to Methods of Rendering Materials Water-Repellent

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British Company having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 The present invention relates to the treatment of materials to render them water-repellent. It is primarily concerned with the production of water-repellent materials by treating bodies with  
15 a composition comprising organo-silicon amines or mixtures of such organo-silicon-nitrogen compounds.

British Specification No. 572,740 describes a process of rendering materials  
20 water-repellent which comprises treating the materials with vapours of an organo-silicon halide. As a hydrogen halide is a by-product of the treatment, the treated products are preferably brought into contact with an alkaline agent such as  
25 ammonia which neutralises any acidity present as a result of the treatment.

According to this invention, a solid article is made water-repellent by a  
30 method which consists in coating the surface of the article with a mixture of organo-silicon amines prepared by reacting an organo-silicon halide with anhydrous ammonia.



The term "organo-silicon amines" as  
70 used herein is intended to cover primary silicon amines such as the organo-silyl amines (organo-silicyle amines)  $R_nSiNH_2$  and the related compounds, such as  $R_nSi(NH_2)_2$ , in which one or two R groups  
75 of the silyl amine are replaced by an amino group, as well as the straight chain and cyclic silazines (secondary amines) characterised by the presence of at least one and usually a plurality of

80  $-Si-NH-Si-$  groups where at least

As starting materials in this invention 35 we prefer to employ organo-silicon halides or mixtures of two or more organo-silicon halides having the average formula  $R_nSiX_{3-n}$  where R represents a hydrocarbon radical, preferably a lower alkyl (e.g. 40 methyl, ethyl, butyl), aryl (e.g. phenyl) alkaryl (e.g. tolyl) or aralkyl (e.g. phenyl-methyl) radical, X represents a halogen atom, preferably a chlorine or bromine atom, and n is a number equal to between 45 0.5 and 3, and is preferably between about 0.7 and 2.8. Mixtures of two different organo-silicon halides, for example mixtures of a methyl silicon 50 halide and a phenyl silicon halide, which mixture meets the above requirements, may also be used.

The organo-silicon amines formed by reacting the organo-silicon halides with 55 ammonia under anhydrous or substantially anhydrous conditions are believed to comprise a complex mixture of silyl-amines,  $R_nSi(NH_2)_{3-n}$  and straight chain and cyclic silazines containing  $Si-NH-$  60 Si linkages. The reactions leading to the formation of these products may be represented by the following equations covering possible reactions between diorgano-  
65 dihalogenosilane (diorgano-silicon dihalide) and ammonia:



one of the free silicon valences of each 85 silicon is connected to a hydrocarbon radical and the remaining valences to nitrogen, or, in the case of a modification of the invention described more fully hereinafter, halogen atoms. In general, the major portion of the reaction products of ammonia and the organo-silicon halides will contain silazine groups. By fractional distillation some of the individual 90 components may be separated one from another. However, for the purposes of the present invention such separation is not necessary. In fact, we prefer to em-

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ploy the mixed organo-silicon amines formed as a result of the ammonia reaction, without further treatment other than the separation of the ammonium halide formed during the reaction and, when desired, the dilution of the amines with suitable inert solvents such as benzene, toluene and ether.

As is shown by the equations given hereinbefore, the reactions between the organo-silicon halide and ammonia are believed to comprise a stepwise conversion of the halide to a silylamine and the condensation of the silylamine to form linear or cyclic silazines. When sufficient ammonia is used to react with all the silicon halide the products will consist substantially of mixed organo-silicon amines. When lesser amounts of ammonia are used the products will include partially reacted organo-silicon halides containing both Si—halide and Si—amine linkages, i.e., compounds such as



where R and X have the meanings given hereinbefore. It is within the scope of the present invention to employ organo-silicon amines and organo-halogeno-silicon amines obtained by reacting organo-silicon halides with ammonia in amounts ranging from that sufficient to react with or replace at least half of the halogen atoms of the organo-silicon halide to that necessary to replace all of the halogen atoms. The products should have a nitrogen-to-halogen ratio of at least 1 and a neutral, or non-acid, action when employed for water-repellency applications. The by-products formed when water-non-repellent bodies are treated with these materials will consist primarily of ammonia or mixtures of ammonium halides and ammonia.

The following specific example is given to illustrate how the present invention may be carried into effect.

#### EXAMPLE.

Under substantially anhydrous conditions, 140 parts of a dimethyldichloromonosilane containing a few per cent. methyltrichloromonosilane was slowly added to 500 parts by volume of liquid ammonia contained in a flask cooled by a dry ice-acetone mixture. After all the chlorosilanes had been added, the excess of ammonia was allowed to evaporate and the reaction products principally comprising

methylpolysilazines were extracted with benzene from the precipitated ammonium chloride. Water-non-repellent bodies treated with the resultant clear, water-white solution of methyl-silicon amines were rendered water-repellent. A clean glass surface was coated with the mixed silicon amines by rubbing a small amount of the solution onto the surface and removing the excess with a clean cloth. An excellent water-repellent surface which resisted the action of acetone, alcohol, or soap and water, was obtained.

Various materials and surfaces such as paper, cotton cloth, wool, ceramic bodies, aluminium, and others specifically mentioned in the aforementioned specification can also be rendered water-repellent by contact with these partial or complete reaction products of an organo-silicon halide and ammonia, the results, in so far as the water-repellent characteristics of the treated products are concerned, being the same as those obtained by use of organo-silicon halides.

When the treating compositions comprise reaction products of organo-silicon halides with a quantity of ammonia insufficient to replace all of the halogen, any ammonium halide remaining on the treated cloth or other material can be removed by washing with water.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of making a solid article water-repellent, which consists in coating the surface of the article with a mixture of organo-silicon amines prepared by reacting an organo-silicon halide with anhydrous ammonia.

2. A method according to Claim 1, in which the organo-silicon halide is a methyl-silicon halide, e.g., dimethyldichloromonosilane.

3. A method according to Claim 1, in which the mixture of organo-silicon amines is employed in a solvent selected from benzene, toluene and ether.

4. A method according to Claim 1, in which the mixture of organo-silicon amines consists of methyl-silicon amines and has an average of between 0.5 and 3 methyl groups per silicon atom.

Dated this 25th day of June, 1945.

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